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Review

Ignition Delay Times of Conventional and Green Hypergolic Propellants at Ambient Conditions: A Comparative Review

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Abstract

Hypergolic propellants have long been central to spacecraft propulsion because of their storability, reliability and rapid ignition. Conventional systems such as hydrazine derivatives paired with oxidisers like nitrogen tetroxide deliver ignition delays in the order of a few milliseconds but pose serious risks due to extreme toxicity and handling hazards. The search for safer and environmentally friendlier alternatives has therefore become a priority in recent years. This review examines ignition delay times reported in the literature for both conventional and green propellants under ambient experimental conditions. Data were collected from published studies between 2000 and 2025 using major scientific databases, including Scopus, Web of Science, and Google Scholar, and are compared across three categories of propellants: traditional hydrazine-based systems, self-igniting ionic liquids and amines, and systems enhanced with catalytic or reactive promoters. The analysis shows that while conventional propellants remain benchmarks with ignition delays typically between 1 and 5 ms, some new formulations, particularly those containing reactive additives such as borohydrides or iodide salts, are achieving similar or improved performance in laboratory tests. The review also highlights that variability in reported ignition delays often stems from differences in test methods, droplet size, oxidiser concentration, and diagnostic approaches. Beyond performance considerations, attention is given to safety and environmental aspects since several green candidates reduce acute toxicity but introduce other challenges, such as instability or corrosive byproducts. By bringing together data in a comparative format and emphasising methodological limitations, this review aims to support the future design and evaluation of practical green hypergolic propellants.

Keywords: hypergolic propellants; ignition delay time (IDT); green propulsion; ionic liquids; reactive promoters; catalytic additives

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1. Introduction

Hypergolic propellants represent a distinct and widely used class of chemical propulsion systems in which the fuel and oxidiser spontaneously ignite upon contact without the need for an external ignition source. This self-ignition capability provides clear operational benefits in rocket propulsion. It allows for simple and reliable engine design, rapid restart capability, and dependable performance in long-duration missions where reliability is critical. Many conventional hypergolic propellants, including hydrazine, monomethylhydrazine (MMH), unsymmetrical dimethylhydrazine (UDMH), and nitrogen tetroxide (NTO), are liquids at ordinary temperature and pressure, which classifies them as

storable liquid propellants. Their storability offers a significant logistical advantage compared to cryogenic propellants such as liquid hydrogen and oxygen that require complex refrigeration systems and boil-off management [1,2].

Although hypergolic ignition occurs spontaneously, it does not occur instantaneously. A finite interval known as the ignition delay time (IDT) exists between the moment of propellant contact and the first visible sign of combustion. This interval is the result of both physical and chemical processes. The physical contribution includes injection, atomization into droplets, mixing, diffusion, and vaporisation, while the chemical contribution reflects the underlying kinetics and reactivity of the fuel–oxidiser pair. Laboratory studies show that liquid phase reactions in some propellants can begin within microseconds, such as 10 to 40 microseconds for MMH with NTO, yet practical ignition delays measured in drop or impinging jet tests are typically several milliseconds [3,4]. This difference highlights the role of physical transport and heat transfer processes as rate-limiting steps that dominate observed IDTs in real systems.

The importance of IDT lies in its direct connection to operational safety and engine reliability. An excessively long IDT allows unburned propellants to accumulate in the chamber, which can result in a violent pressure surge or "hard start" when ignition finally occurs. Conversely, an IDT that is too short can impose damaging thermal and mechanical loads on injectors. For spacecraft propulsion, a finely balanced IDT is required, and values shorter than about 10 ms are generally regarded as acceptable for reliable operation [5,6].

The widespread use of conventional hypergolic propellants has brought undeniable benefits to mission success but also presents severe drawbacks. Hydrazine and its derivatives are highly toxic, corrosive, and carcinogenic. They demand strict handling protocols, specialised facilities, and protective equipment. Nitrogen tetroxide is also hazardous and strongly oxidising. These safety and health concerns are not only operational challenges but also major financial burdens for organisations involved in propulsion system development and launch operations [7,8]. The search for alternatives has therefore been motivated not only by environmental concerns but equally by the desire to reduce occupational hazards and handling costs. In this sense, the label "green" refers to propellants that mitigate the extreme hazards associated with hydrazine class fuels, while recognising that these new formulations may introduce their own safety considerations.

Several research directions have emerged in the pursuit of green hypergolic propellants. One path replaces hydrazine with less toxic energetic salts such as ammonium dinitramide (ADN) and hydroxylammonium nitrate (HAN), which are the basis of well-known systems like LMP-103S and AF-M315E that have undergone flight demonstrations [9–11]. Another path explores ionic liquids and amine-based fuels that can be tailored for hypergolic reactivity while offering reduced vapour toxicity and tuneable properties. Advances in ionic liquid chemistry have revealed that ignition characteristics depend strongly on cation and anion selection, with some boron-containing anions significantly reducing IDT [12,13]. A further approach employs additives or reactive promoters such as metal borohydrides or iodide salts, which react energetically with oxidisers and provide rapid ignition for otherwise non-hypergolic fuels [14,15].

Among the various performance parameters considered in propulsion, ignition delay remains the most commonly reported in laboratory studies. While conventional systems reliably deliver ignition delays of a few milliseconds, the emerging body of research on green propellants shows that several new formulations, particularly when enhanced by reactive promoters, are now approaching or even matching this benchmark under ambient test conditions. However, it is important to note that literature data often vary widely because of differences in experimental methodology, including droplet size and velocity,

oxidiser purity and concentration, and diagnostic methods used to measure ignition [16,17]. This heterogeneity complicates direct comparison and calls for careful interpretation.

Past reviews have provided overviews of green monopropellants and ionic liquids, but a systematic comparative analysis of IDTs across conventional systems, self-igniting green propellants, and promoter-assisted formulations under ambient laboratory conditions has not been presented in a consolidated format [18,19]. This review aims to fill that gap by compiling IDT values from diverse sources, annotating them with experimental details, and providing a comparative synthesis that highlights trends and methodological biases. By presenting the data in this way, the paper seeks to guide future research and encourage standardised testing protocols that will support the safe and practical adoption of green hypergolic propellants in aerospace propulsion.

2. Methods

This review aims to collect and compare IDT data for conventional and green hypergolic propellants measured under ambient laboratory conditions and to annotate each datum with the experimental context that produced it. To achieve this, we carried out a structured literature search using Scopus, Web of Science and Google Scholar. The search covered publications and reports from 2000 to 2025, while important earlier foundational works were included when they were repeatedly cited in reviews or handbooks [1,2]. Example search terms included combinations of hypergolic ignition, ignition delay, monomethylhydrazine (MMH), unsymmetrical dimethylhydrazine (UDMH), nitrogen tetroxide (NTO), hydroxylammonium nitrate (HAN), ionic liquid (IL), borohydride, sodium borohydride, hydrogen peroxide (HTP), catalytic promoter and impinging jet.

After removing duplicates, the initial search returned approximately 350 unique records. Titles and abstracts were screened for relevance, and those clearly outside the scope were removed, leaving 120 papers for full-text review. During full text review, studies were retained if they reported experimental ignition delay values obtained under ambient or near ambient laboratory conditions or if they provided methodological details necessary to interpret previously published IDT values [16,20]. Studies were excluded if they reported only theoretical simulations without experimental validation, if all measured IDT data were obtained exclusively at high pressures or high temperatures outside the ambient scope or if the reported values could not be reliably traced to a primary experimental method or dataset [16,21]. After full text screening, 75 studies supplied usable ambient condition ignition delay data and were included in the comparative analysis. This screening process is shown in Figure 1.

For each included study, we extracted metadata and experimental details into a structured database. The extraction fields were propellant pair or formulation fuel composition oxidiser identity and concentration experimental method such as drop test drop on drop impinging jet open cup or chamber test droplet size or Sauter mean diameter impact or injection velocity diagnostics used for time zero and ignition detection, for example, high speed imaging photodiode pressure transducer or luminosity threshold reported ignition delay value or range number of trials and stated uncertainty ambient test temperature and pressure and any notes on fuel or oxidiser purity additives or promoters and their concentrations. When a publication reported multiple test conditions, each condition was recorded as a separate entry and linked to the primary citation [5,6,22]. Entries that only gave qualitative descriptions were included but explicitly flagged as qualitative so readers can refer to the original source [3,4].

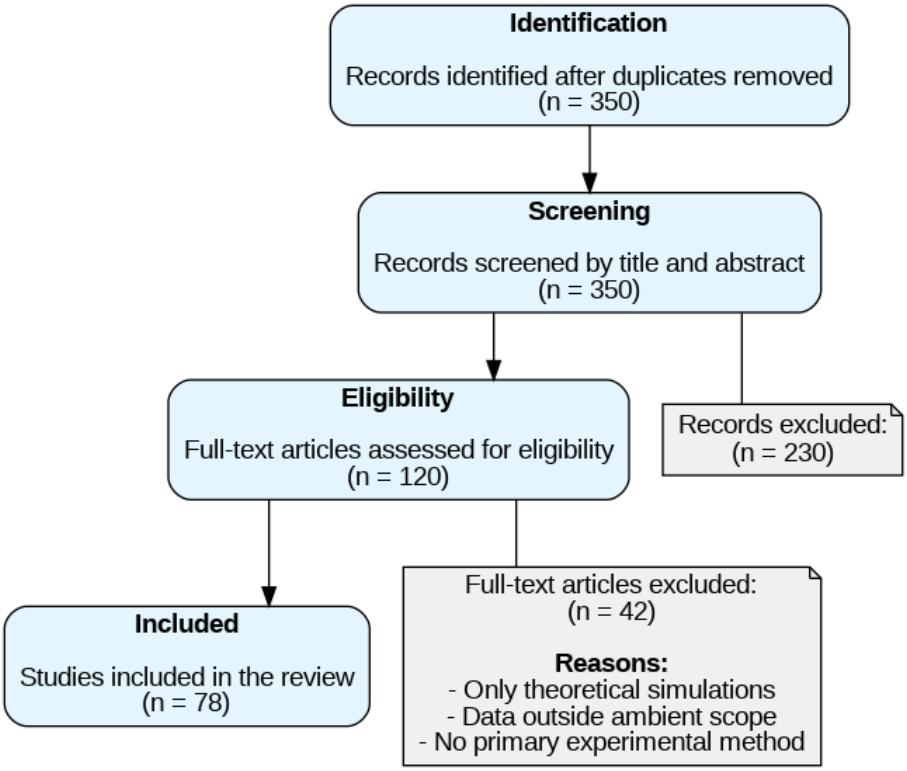

Figure 1. PRISMA-style flow diagram illustrating the literature screening and selection process.

To improve data quality, two independent reviewers screened every extracted record for transcription accuracy and consistency of units. Discrepancies were resolved by consulting the original text or figures and by adjudication between the reviewers. Where numerical IDT values were reported without stated uncertainty, the database records that fact and notes whether values represent single-shot averages or ranges. When multiple numeric values were presented for nominally identical test conditions, the range was preserved, and where possible, the median interquartile range and number of observations were reported rather than forcing a single averaged value [16,17]. We recognised early on that heterogeneity in experimental setups and in definitions of time zero is a major limitation for formal meta-analysis. For this reason, the synthesis focuses on stratified descriptive analysis rather than pooled effect estimates. Where data density and methodological homogeneity allowed, we present grouped summary statistics such as median and interquartile range for a given propellant class and test method. We also use visualisations such as bar graphs and scatter plots stratified by test method and by oxidiser concentration to make methodological biases transparent [16,23].

Finally, any data points that were reported only in secondary sources without a clear primary citation were traced back, where possible, to the original report or removed if provenance could not be established [24,25].

3. Background

3.1. Conventional Hypergolic Propellants and Established Ignition Delay Data

The most common conventional hypergolic propellant combinations pair hydrazine-based fuels with dinitrogen tetroxide or its mixed oxide variants. These propellants have a long operational history because they are liquids at ordinary temperatures and pressures and because they provide reliable and repeatable ignition behaviour. Their storability makes them appropriate for systems that must remain ready for months or years and for missions where cryogenic logistics are impractical [1,2]. Key fuels in this class include

hydrazine, MMH and UDMH. Hydrazine offers high performance but has a relatively high freezing point and handling concerns in pure form. MMH was adopted widely because it improves stability while retaining favourable energetic properties. UDMH is common in several legacy launch systems where low freezing point and robustness are priorities. Aerozine 50, the fifty by weight blend of UDMH and hydrazine, was developed to combine the benefits of both constituents and has a long record of use in programmes such as Apollo and Titan II [1,2,26]. Mixed oxides of nitrogen MON variants are used to lower oxidiser freezing points at the expense of some handling complexity and increased vapour pressure. Red fuming nitric acid RFNA was used historically in tactical systems and remains relevant in legacy ignition studies [27].

IDT is a central design metric for these conventional systems, and a substantial body of ambient condition data exists. MMH with NTO is frequently treated as the benchmark. High-speed optical diagnostics and focused laboratory tests show that liquid phase chemical induction can begin within microseconds for strong oxidiser pairs, while the macroscopic ignition delay observed in practical drop tests is usually in the millisecond range [22,28]. Representative ambient drop test values for MMH with NTO cluster around 1–3 ms, with a commonly cited controlled measurement of about 1.45 ± 0.60 ms [29]. MMH with RFNA displays larger variability in drop tests with reported IDTs from roughly 2.5 to 10.5 ms, depending on test details and oxidiser concentration and with liquid phase induction still measured in tens of microseconds in high-resolution studies [27]. UDMH with NTO and Aerozine50 with NTO are generally reported to yield IDTs of a few milliseconds in engineering practice, although modern laboratory tabulations for some of these historical systems are less extensive than for MMH/NTO [2,26].

Some alternatives explored for lower toxicity illustrate the trade-off inherent in replacing hydrazine-class fuels. For example, DMAZ tested with N_2O_4 showed much longer ignition delays in ambient open cup tests of about 68 ms, which demonstrates that reduced toxicity can come with significant performance penalties unless further formulation or promotion is used [30]. When reviewing conventional IDT values, it is important to bear in mind that the experimental context influences each number. The tables (Tables 1 and 2) in this review, therefore, annotate each entry with the primary reference and the key test conditions so readers can compare like with like [22,27].

Table 1. Representative IDTs for conventional hydrazine class propellant pairs at ambient conditions.

Propellant Combination	IDT (ms)	Conditions (Temp, Pressure, Method)	Source	Notes
MMH/NTO	1.45 ± 0.60	Ambient (drop test, oxidiser dropped from 2.5 inches height)	[3,31]	Liquid phase induction delay: 10–40 µs
MMH/NTO	1–3 (typical range)	General (various methods)	[2,4,32,33]	Widely used in US spacecraft
UDMH/NTO	Few milliseconds (typical)	General (various methods)	[1,2]	Widely used in Russian rockets
Aerozine 50/NTO	Short and repeatable	General (various methods)	[1,2]	Widely used (Apollo, Space Shuttle, Dragon)
MMH/RFNA	2.5–10.5	Ambient (drop test, varied by impact point)	[5]	Liquid phase induction delay: 30–100 µs. Note: Impinging jet tests reported *no ignition*
DMAZ/N_2O_4	68	Ambient (open cup test)	[1,2]	Considered a less toxic alternative to hydrazine derivatives

Table 2. IDTs of Self-Igniting Green Hypergolic Propellants at Ambient Conditions.

(a) Ionic Liquids with H_2O_2 (HTP)				
Propellant Combination	**IDT (ms)**	**Conditions (Temp, Pressure, Method)**	**Original Source**	**Notes**
[EMIM]/96.1% H_2O_2	26–32	Ambient (drop test)	[34]	Thiocyanate anion-based IL
[EMIM] + 5 wt% Copper Thiocyanate/96.1% H_2O_2	~13	Ambient (drop test, impinging injector)	[34]	Copper additive significantly reduces IDT
Alkyl-substituted thiocyanate ILs/H_2O_2	~45	Ambient (drop test)	[35]	Longer alkyl chains increase IDT
[EPy] (IL-24)/97.4% H_2O_2	26.8	Ambient (drop test)	[36]	Pyridinium-based thiocyanate IL, shorter alkyl chains improve IDT
[HIM] (IL-30)/H_2O_2	7.3	Ambient (drop test)	[37]	Protic thiocyanate IL, solid at ambient conditions
HIM-35 (35 wt% [HIM] + 65 wt% [EMIM])/H_2O_2	16.7	Ambient (drop test)	[37]	Liquid blend, avoids metallic additives
(IL-38)/H_2O_2	30.8	Ambient (drop test)	[38]	Trialkylsulfonium thiocyanate IL, IDT increases at lower temperatures
[EMIM] (IL-17)/95% H_2O_2	18.5	Ambient (drop test)	[39]	Borohydride anion-based IL, solid at ambient conditions
(IL-2)/90–98% H_2O_2	<30	Ambient (drop test)	[18]	Borohydride anion-based IL
Novel Borohydride ILs with Organic Super-bases/90% H_2O_2	28.3	Ambient (drop test)	[40]	Hybrid borohydride design
(b) Ionic Liquids with WFNA				
Propellant Combination	**IDT (ms)**	**Conditions (Temp, Pressure, Method)**	**Original Source**	**Notes**
[EMIM] [C_2N_3]/WFNA	52	Ambient (drop test)	[41]	Dicyanamide anion-based IL
[EMIM] [C_2N_3]/WFNA	35	Ambient (drop test)	[41]	Dicyanamide anion-based IL
[EMIM] [C_2N_3] or [C_2N_3] + AMPZ/WFNA	~20	Ambient (drop test)	[41]	AMPZ additive significantly reduces IDT

3.2. Green Hypergolic Propellants: Advances in Self-Igniting Catalytic and Reactive Systems

Research on green hypergolic propellants aims to reduce the health and handling burdens associated with hydrazine-class fuels while retaining acceptable performance. Two broad strategies have emerged. Self-igniting propellants are intrinsically hypergolic with a chosen oxidiser and include certain ionic liquids and designer amines. Promoter-dependent systems rely on catalytic or reactive additives to induce or accelerate ignition in otherwise non-hypergolic fuels. An important driver in this field is the use of less toxic oxidizers, with High-Test Peroxide (HTP, H_2O_2) being a leading candidate due to its high density, high oxygen content, and significantly lower handling toxicity compared to nitrogen oxides. Both approaches have advanced rapidly, but they bring different compromises and technical challenges [42,43].

Self-igniting ionic liquids are promising because they have negligible vapour pressure, tuneable density and structural flexibility that allows chemists to tailor ignition characteristics. Thiocyanate anion-based ionic liquids and borohydride anion-based ionic liquids are among the most studied with concentrated hydrogen peroxide as oxidiser. Reported ambient IDTs for these IL families span from a few milliseconds to several tens of milliseconds, depending on cation and anion choices, oxidiser purity and temperature. For example, a

blended protic and aprotic thiocyanate mixture, HIM-35, produced an ambient drop test IDT of about 16.7 ms, while a protic thiocyanate IL measured as low as 7.3 ms but was solid at room temperature and thus required blending for practical use [43,44]. Borohydride anion ILs demonstrate comparable IDT ranges with some candidates recorded below 30 ms under high concentration peroxide, but many require formulation work to remain liquid at ambient temperatures [42].

Figure 2 visually distinguishes between the two primary mechanisms by which additives promote hypergolic ignition in green propellants. Promoter-dependent approaches are split into catalytic and reactive pathways.

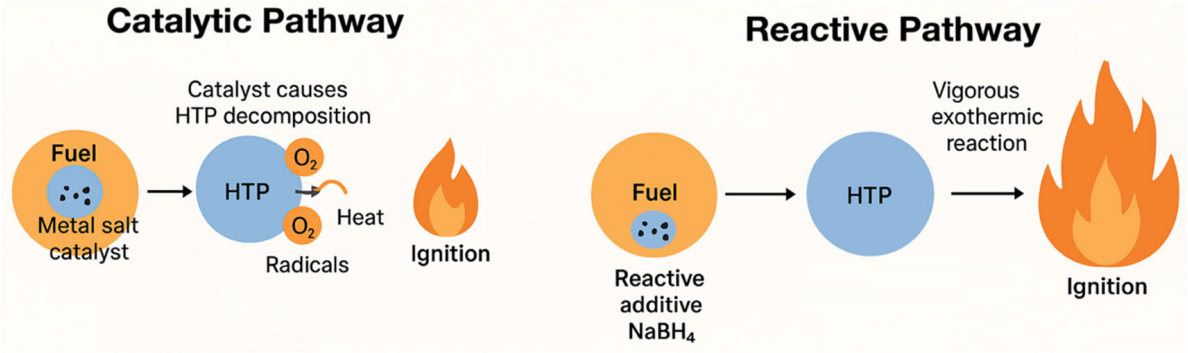

Figure 2. Schematic of Catalytic vs. Reactive Ignition Mechanisms.

3.2.1. Catalytic Pathway

Catalytic promoters function by dissolving an additive, typically a metal salt, into the fuel. Upon contact with an oxidiser like HTP, the catalyst rapidly accelerates the oxidiser's decomposition. This process generates heat and a high concentration of reactive radical species, which collectively raise the temperature of the surrounding fuel to its auto-ignition point. While catalytic systems can substantially shorten ignition delays, they often remain above the 10 ms threshold and may introduce metallic combustion residues that can reduce specific impulse or complicate materials compatibility [44].

3.2.2. Reactive Pathway

Reactive promoters, such as sodium borohydride ($NaBH_4$) and boron-based additives, operate through a different mechanism. These additives are highly energetic reducing agents that undergo a vigorous, direct, and exothermic reaction with the oxidiser upon contact. This initial reaction serves as a powerful ignition source, releasing a significant amount of energy that rapidly triggers the combustion of the bulk fuel. For example, kerosene-based gel fuels with sodium borohydride have shown ambient drop test IDTs near 4–5 ms, and gelled ethanol with boron particles has been reported to ignite in about 1.3 ms under controlled conditions [45]. Reactive promoter systems, therefore, represent a critical route to match or exceed conventional propellant performance, but they introduce their own storage and handling constraints because many reactive additives are moisture-sensitive and can degrade over time [42,43].

4. Results

4.1. Conventional Propellants

Conventional hydrazine-class propellants remain the most extensively documented group in the ambient ignition literature, and they serve as the practical benchmark for ignition delay performance. The literature shows that MMH with NTO is the single most frequently reported fuel oxidiser pair and controlled ambient drop tests for this combination

typically return ignition delays in the one to three millisecond range, with a well-cited controlled measurement at about 1.45 ± 0.60 ms [29]. Detailed high-speed diagnostics reveal that liquid phase chemical induction for strong oxidiser pairs can begin on the order of tens of microseconds, but the macroscopic ignition delay observed in engineering tests reflects the slower physical processes of atomization, vaporisation and mixing, which usually place the measured delay in the millisecond regime [22,28].

Unsymmetrical dimethylhydrazine paired with nitrogen tetroxide exhibits broadly similar behaviour, although fewer ambient drop test data are reported openly. Engineering summaries and legacy handbooks commonly place UDMH with NTO in the same performance class as MMH with NTO and describe ignition delays in the order of a few milliseconds, which explains the widespread operational use of these fluids in legacy and contemporary systems [1,2,26]. Aerozine 50, the fifty-to-fifty blend of hydrazine and UDMH, was developed to combine favourable energetic properties with improved low-temperature performance. Its long operational pedigree in systems such as the Apollo lunar module and Titan II family has left a historical record that characterises it as producing short and repeatable ignition delays suitable for operational use, even if modern high-resolution numerical IDT values are less frequently tabulated in recent publications [2,26].

Older nitric acid oxidisers and their mixed oxide variants introduce more scatter into ambient IDT values. For example, MMH with red fuming nitric acid has been reported to show drop test ignition delays that range from approximately 2.5–over 10 ms, depending on test geometry impact point and acid concentration, and impinging jet experiments on the same nominal fluids have on occasions failed to produce ignition, which highlights the strong influence of experimental configuration on apparent hypergolicity [27].

Emerging single-component replacements for hydrazine, such as DMAZ paired with N_2O_4, have demonstrated the essential trade-off that motivates green research; open cup testing of DMAZ with N_2O_4 returned ignition delays near 68 ms, which is far slower than conventional hydrazine class systems and therefore not acceptable for many high-performance spacecraft applications without additional promoters or structural modification [30,33]. Taken together, the conventional dataset forms a dense cluster in the one to three millisecond band, and this clustering defines the reference regime that designers and researchers use when they evaluate alternative propellant concepts [1,2,26].

Figure 3 provides a comprehensive visual summary of the IDTs for a wide range of conventional and green hypergolic propellant combinations at ambient conditions. The bar chart is organised into three categories, Conventional, Self-Igniting Green, and Promoted Green, to facilitate a direct comparison of their performance. The red dashed line at 10 milliseconds represents the critical threshold for avoiding "hard start" combustion and ensuring stable thruster operation, which is a key performance criterion in aerospace applications. The figure highlights the significant progress of green propellants in achieving competitive IDTs. While the conventional MMH/NTO system sets a benchmark with an IDT of 1.45 ± 0.60 ms, and some self-igniting ionic liquids like [HIM]/H_2O_2 also fall below the 10 ms threshold, the most striking finding is the performance of the promoter-dependent systems. Reactive promoted fuels like Gelled ethanol with boron particles and Ethylenediamine with hybrid additives, with IDTs of 1.33 ms and 2.69 ms, respectively, demonstrate performance on par with or even superior to conventional toxic propellants. This visual data powerfully reinforces the paper's central argument that advanced green propellant formulations are now viable alternatives to conventional toxic systems.

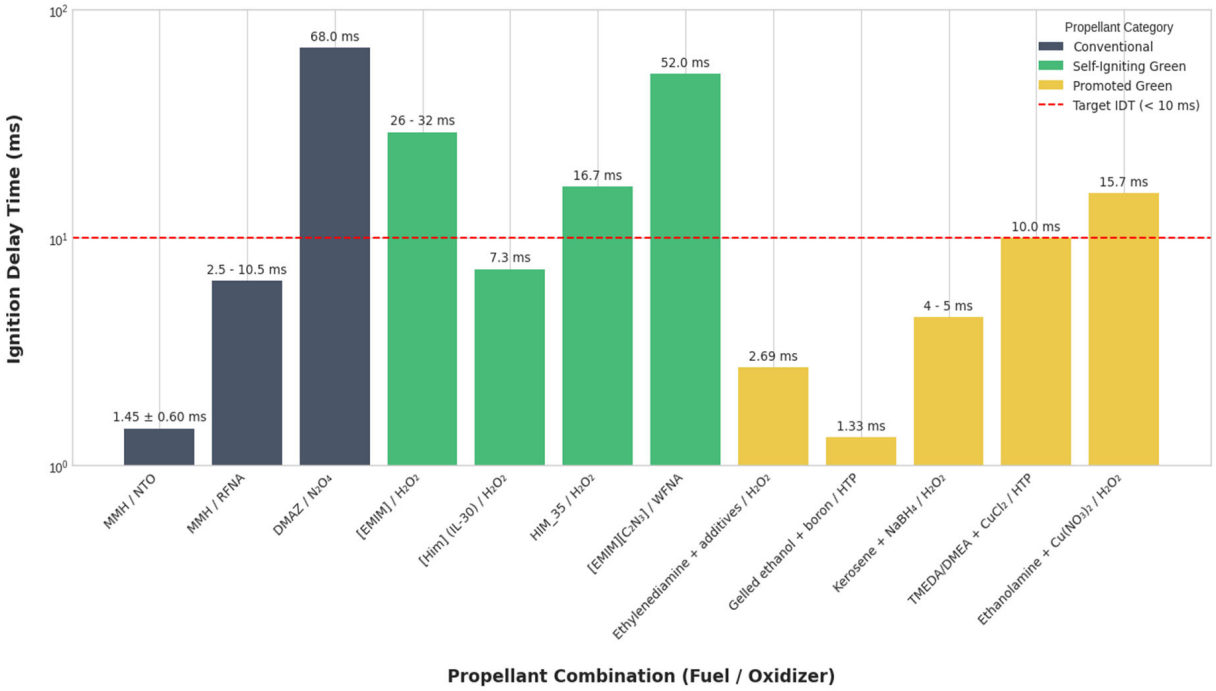

Figure 3. Comparative IDTs of Hypergolic Propellants. The red dashed line represents the <10 ms target IDT often cited for high-performance applications.

4.2. Self-Igniting Ionic Liquids and Amine-Based Fuels

Self-igniting green propellants, most commonly energetic ionic liquids and designer amines, occupy a broader and more heterogeneous region of performance space than conventional hydrazines. Ionic liquids offer molecular tunability that allows chemists to adjust viscosity, density, volatility and chemical reactivity by changing cation and anion combinations, and the open literature contains many examples that illustrate how such tuning maps onto ignition behaviour [42,43].

Among ionic liquids, the thiocyanate anion family and the borohydride anion family have attracted the most study. Thiocyanate-based ionic liquids have displayed a wide range of ambient condition IDTs. For instance, a protic thiocyanate ionic liquid reported an ambient drop test IDT near 7 ms, but it was a solid at room temperature, so its direct applicability as a liquid propellant is limited unless blended with an aprotic counterpart [44]. Blends such as HIM-35 that combine protic and aprotic thiocyanates have been formulated to solve the phase problem and produce a room temperature liquid with a measured IDT near 16.7 ms, which shows that blending is a practical pathway to balance handling and ignition performance [43,44]. In contrast, alkyl-substituted thiocyanate ionic liquids with longer chains often show significantly longer delays, for example, reported values near 45 ms, which underscores the sensitivity of ignition behaviour to relatively small structural changes in the cation [44]. Borohydride anion-based ionic liquids similarly show promising self-ignition with high-concentration hydrogen peroxide oxidisers and, in some cases, produce IDTs below 30 ms, but again, many of the most reactive borohydride salts are solid at ambient temperature and require formulation work to be practical [12,46].

Tables 2–4 summarise representative ambient condition IDT measurements for a selection of green propellant systems and promoter strategies found in the surveyed literature.

Table 3. IDTs of Catalytically Promoted Green Hypergolic Propellants at Ambient Conditions.

Propellant Combination	IDT (ms)	Conditions (Temp, Pressure, Method)	Original Source	Notes
Ethanolamine + 9% $Cu(NO_3)_2 \cdot 3H_2O$/90% H_2O_2	15.7	Ambient (drop test)	[41]	Amine-based catalytic system
TMEDA/DMEA + CuCl2/HTP	~10	Ambient (impinging jet)	[41]	Amine-based fuel with Cu catalyst
Gel fuel + catalyst/90% H_2O_2	10–50	Ambient (drop test)	[47]	Widespread due to mixing sensitivity

Table 4. IDTs of Reactively Promoted Green Hypergolic Propellants at Ambient Conditions.

Propellant Combination	IDT (ms)	Conditions (Temp, Pressure, Method)	Original Source	Notes
Ethylenediamine + 10 wt.% $NaBH_4$: NaI/95% H_2O_2	2.75	Ambient (drop test)	[48]	Hybrid reactive/catalytic additives
Ethylenediamine + 10 wt.% $NaBH_4$:NH_4I/95% H_2O_2	2.69	Ambient (drop test)	[48]	Hybrid reactive/catalytic additives
Kerosene-based gel fuel + $NaBH_4$/90% H_2O_2	4–5	Ambient (drop-on-drop test)	[14,49]	Metal hydride additive
Gelled ethanol + boron particles/HTP	1.33	Ambient (drop test)	[15]	Boron particle additive

Dicyanamide-based ionic liquids and related anion families tend to yield even longer ambient delays when paired with nitric acid oxidisers, though additives such as amino-substituted heterocycles can reduce IDT substantially by introducing reactive bonds that mirror those in classic hydrazine chemistry [25,50]. The overall picture from the literature is that ionic liquids can be engineered to approach acceptable ignition delays. However, it is important to contextualise the ignition delay requirements. While the <10 ms threshold is a critical benchmark for high-performance applications demanding rapid and repeatable restarts, longer delays of up to 50 ms may be entirely sufficient for other uses, such as in-space attitude control or orbital manoeuvring systems where absolute reliability is more critical than millisecond-level responsiveness. Many single-component ILs still exhibit IDTs at or above the 10 ms mark, which means that either further molecular refinement or admixture with promoters is needed to meet the most stringent performance requirements. Temperature dependence also plays an important role, and several studies show that IDT increases at low temperature, while some trialkylsulfonium thiocyanate ILs maintain hypergolicity even at sub-zero temperatures with an expected penalty to delay [38].

4.3. Catalytically Promoted Systems

Catalytic promotion has been explored extensively as a way to shorten ignition delays while retaining relatively benign base fluids. The catalytic pathway usually involves dissolving a transition metal salt in the fuel so that upon contact with an oxidiser such as high-test hydrogen peroxide, the catalyst accelerates oxidiser decomposition. The resulting release of oxygen radicals and heat brings the local fluid temperature to the point where the fuel can auto-ignite [17,23,51,52]. In practice, catalytic strategies often halve or reduce significantly the ignition delay of the base fluid, but they rarely produce sub 10 ms performance on their own. Several representative experimental reports show that putting a few wt.% of copper thiocyanate into an imidazolium thiocyanate ionic liquid reduces ambient drop test IDT from the mid to high 20 ms down to approximately 13 ms, which is a

substantial improvement yet still above the informal 10 ms threshold that many designers use to avoid hard starts [34,36,37,44].

Amine-based formulations with copper nitrate or copper chloride catalysts also demonstrate fast ignitions in the order of 10–16 ms, depending on the diagnostic and injection geometry, and impinging jet tests with carefully tuned injector parameters have produced values nearing 10 ms in a few controlled studies [53–55]. The literature also records practical drawbacks to catalytic methods. Metal salts can separate over storage durations, leading to inconsistent performance, and metallic combustion residues may reduce specific impulse and deposit on downstream components, which raises long-term materials compatibility concerns [56]. These trade-offs mean catalytic routes are attractive for systems where slight increases in complexity can be tolerated in exchange for lower base fluid toxicity, but they may not be ideal where residues and contamination are unacceptable.

4.4. Reactively Promoted Systems

Reactive promotion stands out in the ambient literature as the most direct pathway to achieve ignition delays that match or exceed those of conventional hydrazine systems. Reactive promoters are highly reducing additives that undergo vigorous exothermic reactions with oxidisers in the liquid phase, generating heat radicals and gaseous products that trigger the main fuel to combust rapidly [39,57,58]. Examples in the literature show that kerosene based gel fuels with sodium borohydride can produce ignition delays around 4 to 5 ms in drop on drop tests, and gelled ethanol formulations energised with boron particles have been reported to ignite in as little as about 1.3 ms under specific ambient conditions, which is faster than many measurements reported for MMH with NTO in similar test geometries [14,47,59].

Hybrid additive strategies that combine a reactive reductant such as sodium borohydride with an iodide salt or with a small catalytic component have provided some of the most compelling ambient results. For example, ethylenediamine formulations with 10 wt.% of a $NaBH_4$ and NaI blend have yielded mean IDTs near 2.7 ms, and similar blends with NH_4I have given values around 2.69 ms under controlled drop test conditions [48,49,60]. These experiments illustrate that additives can transform non-hypergolic base liquids into high-performance hypergolic fuels. The practical caveat for reactive promoters is sensitivity to moisture and handling constraints; many reactive additives are deactivated by water or hydrolyze over storage, so specialised drying or encapsulation strategies are required to make field-ready formulations. Moreover, combustion residues from metallic additives and the consequences for engine maintenance and life must be evaluated carefully.

Figure 4 compares the IDT of a base fuel (grey circles) with its performance when a promoter is added (green circles), visually demonstrating the dramatic shift in performance. This scatter plot provides a quantitative and novel perspective on the effectiveness of catalytic and reactive promoters in enhancing hypergolicity. For the [EMIM]/H_2O_2 system, a catalytic additive ([EMIM] + CuSCN) reduces the IDT from an intrinsically slow igniting 29 ms to a much more competitive 13 ms.

More significantly, the figure shows how promoters can induce hypergolicity in otherwise non-hypergolic propellants. Both Ethylenediamine and Hydrazine, with baseline IDTs of 100 ms and 250 ms, respectively, fail to meet the hypergolic standard on their own. However, with the addition of hybrid additives, their IDTs are reduced to very low values (2.69 ms and 5.5 ms), well below the 10 ms target. This figure provides a clear visual proof of the power of molecular design and additive engineering in changing the ignition characteristics of green propellants, turning underperforming or non-hypergolic candidates into highly viable alternatives.

Figure 4. The Impact of Additives on IDTs. The plot shows how promoters can drastically reduce the IDT of a base fuel or induce hypergolicity in fuel/oxidiser pairs that are otherwise too slow to be practically useful. The label "Non-Hypergolic" reflects that while ignition does occur, the delay is unacceptably long.

4.5. Methodological Sensitivity and Diagnostic Effects

A pervasive theme in the dataset is that reported ignition delays cannot be interpreted without clear attention to experimental method and diagnostic definition. Time zero may be defined as first liquid contact, first visible luminosity or first pressure rise, and these choices materially change the numeric IDT reported [16,61,62]. Drop tests are simple and widely used for baseline screening, but they are sensitive to droplet size, impact location and relative momentum. Impinging jet tests mimic injector impingement and shear-based mixing more closely and, in some cases, show earlier ignition, while in other configurations, they fail to ignite fluids that do ignite in drop tests [5,22]. Open cup and chamber level tests produce larger mixing scales and typically show longer delays. Diagnostic resolution adds another layer of complexity. High-speed imaging and photodiode recordings can reveal microsecond-scale induction phenomena that are invisible to slower pressure probes or visual observation [63,64]. The MMH with RFNA discrepancy that appears in several studies is a clear example. Drop tests under certain conditions report delays in the millisecond band, while impinging jet rigs with different mixing dynamics have failed to ignite, which means that a nominally hypergolic pair may or may not function in a given engine geometry [5,65]. To assist the reader and to allow fair comparisons across the literature, this review includes method descriptors for every tabulated IDT, such as test type, droplet size, oxidiser wt.% and diagnostic technique, and entries that lack sufficient methodological detail are flagged.

A comparative analysis of the data reveals clear trends regarding these experimental variables. Firstly, droplet size has an inverse relationship with IDT; smaller droplets, with their higher surface-area-to-volume ratio, consistently exhibit shorter delays due to more rapid heating and vaporisation. Secondly, oxidizer concentration is a dominant factor, with higher concentrations of H_2O_2 or WFNA drastically reducing IDTs by increasing the rate of initial decomposition and exothermic reactions. Finally, the diagnostic method introduces systematic variance; photodiodes often record the shortest IDTs as they are sensitive to the first light emission, while high-speed video analysis may yield slightly longer times depending on the visual definition of ignition, and pressure transducers typically record the

longest delays as they measure the bulk effect of gas production. These factors collectively account for much of the variability seen in the literature for similar propellant combinations.

4.6. Quantitative Synthesis and Comparative Ranges

Bringing together the extracted records allows a quantitative summary that is useful for designers and researchers. Conventional hydrazine class propellants form a tight cluster with most ambient drop test IDTs lying between 1 and 3 ms band and with well-documented liquid phase induction measured in the tens of microseconds. Self-igniting ionic liquids form a broader distribution that typically spans roughly 7 to 50 ms, with the fastest protic species near 7 ms and many practical liquids or blends in the 10 to 30 ms range. Catalytically promoted systems commonly occupy the 10 to 20 ms region after additive incorporation, while reactively promoted systems concentrate in the 1 to 5 ms band with notable entries below 3 ms. These broad ranges should not be interpreted as immutable categories; rather, they represent current experimental evidence, and they will change as more studies with standardised reporting appear. It is also important to note that statistical robustness is uneven. Conventional systems are supported by extensive data and by operational experience, whereas many green propellant reports are limited to single laboratory studies without independent replication. This asymmetry suggests caution in extrapolating early positive findings for green systems into system-level readiness assessments.

4.7. Data Gaps and Priorities

The assembled literature surface reveals several clear gaps that must be addressed if green propellants are to be advanced toward operational use. Few studies perform inter-laboratory verification, so the reproducibility of many reported IDTs remains untested. Temperature dependence is underexplored in many IL families and in promoter systems, and systematic ageing or storage stability studies are often absent. Toxicology and ecotoxicology data are rarely reported alongside ignition performance metrics, which makes it hard for programme managers to balance performance gains against health and environmental effects. Finally, material compatibility testing with realistic tank and valve materials is insufficiently represented in the ambient literature, yet it is essential for flight readiness. The next research phase should prioritise standardised tests across multiple laboratories, expanded temperature and ageing matrices and integrated assessments that pair IDT performance with toxicity and compatibility metrics.

5. Discussion

5.1. Interpretation of Trends

One of the clearest outcomes from the reviewed dataset is the strong dependence of IDTs on the methodology employed. Reported IDTs vary not only with the choice of diagnostic but also with droplet size, injection geometry, oxidiser concentration, and definition of ignition onset. For example, the well-documented discrepancy for MMH with red fuming nitric acid, where ignition was observed in drop tests but not in impinging jet tests, demonstrates that laboratory screening data may not always reflect realistic injector conditions [5,20]. Similarly, studies using open cup tests often return longer delays due to larger liquid volumes and slower mixing [16]. High-speed imaging and photodiode diagnostics reveal chemical induction events on the order of microseconds that are entirely invisible when ignition is defined by chamber pressure rise [17,22]. This methodological diversity complicates comparison and emphasises the urgent need for standardised reporting protocols. Without common definitions of time zero and ignition criteria, data synthesis across laboratories will continue to suffer from artificial scatter. For green propellants in

particular, where performance margins are still under scrutiny, the development of shared experimental benchmarks is as important as molecular innovation [66].

The literature provides compelling evidence that molecular design and additive incorporation are decisive in shaping ignition behaviour. The presence of functional groups such as N–N bonds, as seen in additives like AMPZ, has been shown to lower ignition delays in dicyanamide ionic liquids by facilitating early radical chemistry [41,63]. Similarly, shorter alkyl chains on cations in thiocyanate ionic liquids consistently correlate with faster ignition, while protic cations produce especially short delays but introduce challenges of phase stability [37,38]. These observations indicate that ignition delay is not merely a bulk property but is intimately tied to the fine chemical structure of the fuel [67,68]. Catalytic additives extend this principle by accelerating oxidiser decomposition [18,34], while reactive additives like sodium borohydride directly release energy that couples into ignition of the base fuel [14,46]. The demonstrated ability to transform non-hypergolic amines into highly competitive fuels through additive engineering underscores the value of a rational design framework where chemical reactivity principles guide the synthesis of next-generation propellants rather than reliance on empirical trial and error [43,69].

5.2. Trade-Offs and Limitations

Although reactive promoted systems currently achieve the most attractive ignition delays, they introduce new challenges that cannot be ignored. These observations reveal the central engineering dilemma of green hypergolic propellants: the best ignition performance is often achieved by formulations that are less robust in handling and storage, while the most stable and convenient formulations tend to lag in ignition performance. The challenge for future work is to strike a balance between these competing priorities, with equal weight given to stability, storability, and combustion efficiency alongside ignition delay [21,70].

In addition, the shift away from highly toxic hydrazines, while beneficial, introduces a new set of risks that must be managed. For instance, reactive promoters like sodium borohydride and other metal hydrides are highly sensitive to moisture and degrade on contact with water, which raises concerns about storage stability and handling safety [15,48]. Boron additives that drive ignition delays below 2 ms can leave combustion residues that reduce specific impulse and foul hardware surfaces [30,60,71]. Catalytic systems offer cleaner combustion but often fall short of the sub-ten millisecond threshold required for stable engine operation [71]. Similarly, many of the most promising ionic liquids are solids at ambient temperature, making them impractical as stand-alone fuels unless blended. Furthermore, while new compounds may have lower acute human toxicity, their long-term environmental persistence and ecotoxicology are often not well characterised, representing a critical knowledge gap.

In practice, the ignition delay requirements for spacecraft propulsion are shaped not only by the desire to avoid hard starts but also by mission-specific operational margins. Thrusters in the 1–3 ms band, as achieved by MMH with NTO, are reliable for repeated firings over long mission durations. Green propellants that achieve 5 ms ignition delays may in many cases be sufficient, particularly for smaller satellites and attitude control thrusters, but operational adoption will depend on confidence in repeatability and stability over thousands of cycles [10,72]. The results indicate that reactive promoter systems already meet the performance criterion, but the absence of long-term cycle testing means that their readiness remains unproven [73]. Until green systems demonstrate both performance and reliability under realistic duty cycles, conventional hydrazine fuels will continue to dominate mission-critical applications [19].

Balancing Performance and Safety in Future Design

Future research must holistically address the trade-off between performance and safety. A promising direction is the encapsulation of reactive additives like $NaBH_4$ in protective polymer shells, which could improve storage stability without compromising reactivity upon injection. At the molecular level, efforts should focus on designing single-component ionic liquids that are liquid at ambient temperatures (enhancing handling safety), have low viscosity, and possess intrinsic chemical functionalities that promote rapid ignition without requiring unstable additives. Ultimately, an integrated design approach is needed, where material compatibility, long-term stability, and toxicological screening are conducted in parallel with performance testing, not as an afterthought.

5.3. Research Gaps and R&D Directions

Despite rapid progress, the review reveals persistent gaps in the dataset. Independent replication of results is rare, and most green formulations are reported by single research groups without external confirmation. Temperature dependence remains poorly mapped, with only a handful of studies extending testing below freezing, despite the fact that many spacecraft operate in such conditions [36,38]. Long-term storage stability and compatibility with common tank and valve materials are seldom examined. Finally, toxicity data are rarely published alongside ignition data, which prevents a balanced assessment of whether the green label is truly justified [7,74]. The absence of comprehensive safety and handling studies risks creating a situation where ignition delay improvements overshadow equally important operational hazards [42,75].

Addressing these gaps requires a more integrated research strategy. Standardisation of ignition delay testing should be a community priority, with agreed definitions of ignition onset, droplet or injector geometry, oxidiser concentration, and diagnostic methods. Shared reference propellants could be adopted to calibrate laboratories against one another. At the molecular level, further work should pursue the design of ionic liquids that combine liquid phase stability at ambient conditions with intrinsically short ignition delays, potentially through the introduction of reactive protic groups or hybrid anions. For promoter systems, encapsulation and protective coating strategies may improve the storage stability of sensitive additives such as $NaBH_4$. Hybrid promoter formulations that combine catalytic and reactive elements warrant further study, given their ability to deliver ignition delays of >3 ms while maintaining tunability. Most importantly, future studies should integrate ignition delay testing with toxicity, environmental persistence, and material compatibility assessments [70]. Only by combining performance data with safety and handling metrics can the field ensure that new formulations are not just fast-igniting but also genuinely safer and more sustainable alternatives to hydrazine [19,74].

6. Conclusions and Outlook

This review compiles and interprets IDT data for conventional and emerging green hypergolic propellants under ambient conditions. The primary finding is that while conventional hydrazine-based systems remain the benchmark with IDTs of 1–3 ms, significant advancements in green propellant chemistry, particularly through the use of reactive promoters, have produced formulations with comparable or even superior ignition performance.

Key conclusions from this review are as follows:

- **Performance Benchmark:** Conventional MMH/NTO systems reliably achieve IDTs in the 1–3 ms range, establishing the target for green alternatives.
- **Promoters are Key:** Reactive promoters (e.g., $NaBH_4$, boron particles) are the most effective strategy for achieving sub-5 ms IDTs in green fuels, successfully transforming non-hypergolic base fuels into high-performance options.

- **Ionic Liquids Show Promise:** Molecular tuning of ionic liquids offers a pathway to intrinsically hypergolic fuels with reduced toxicity, although many current formulations require blending or additives to meet the most aggressive performance targets.
- **Methodology Matters:** Reported IDT values are highly sensitive to experimental methodology. Standardised testing and reporting protocols are urgently needed for meaningful cross-study comparisons.
- **New Challenges Emerge:** The transition to green propellants introduces new challenges, including storage stability of reactive additives, combustion residues, and unknown long-term environmental impacts, which must be addressed for flight readiness.

Future research should prioritise inter-laboratory benchmarking, long-term ageing studies, and integrated assessments that combine performance metrics with toxicity and material compatibility data. With a coordinated effort, green hypergolic propellants, especially reactively promoted systems, are strong candidates to replace hydrazine in a growing number of space missions over the next decade.

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Nomenclature

ADN	Ammonium Dinitramide
HTP	High-Test Peroxide
HAN	Hydroxylammonium Nitrate
IDT	Ignition Delay Time
IL	Ionic Liquid
MMH	Monomethylhydrazine
NTO	Nitrogen Tetroxide (Dinitrogen Tetroxide)
RFNA	Red Fuming Nitric Acid
UDMH	Unsymmetrical Dimethylhydrazine
WFNA	White Fuming Nitric Acid

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